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Synthesis of Novel Azo Fused Dipyrazolopyridine Derivatives using Waste Orange Peel Derived C-SO_3H Nano-Powder as an Efficient and Reusable Catalyst.

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Abstract

A new series of structurally diverse azo fused dipyrazolopyridines has been synthesized via one pot pseudo six component reaction of various substituted aryl azo-salicylaldehydes with ethyl acetoacetate, hydrazine hydrate and ammonium acetate using waste orange peel derived carbon modified sulfonic acid (C-SO_3H) as a mild, efficient and inexpensive heterogeneous catalyst. The prepared catalyst was characterized by FT-IR, XRD, SEM, EDX and XPS studies. The catalytically synthesized compounds were characterized by FT-IR, ^1H NMR and ^{13}C NMR. Use of recyclable powder catalyst (C-SO_3H) for the excellent yields with rapid formation of the targeted azo fused dipyrazolopyridines with simple work-up procedure are the notable advantages of this protocol.

Keywords: *Waste orange peel, Solid acid catalyst, Greener catalyst, Dipyrazolopyridines.*

1. INTRODUCTION

The exploitation of solid heterogeneous catalysts deliver innovative methods in the field of green catalysis by enhancing efficiency, selectivity and effective role in the modern synthetic organic field (Kumar et al. 2014; Kandepi and Narender, 2012). In the recent scenario, the invention of new kind of carbon materials such as carbon nanotubes, carbon dots and ordered mesoporous carbons (Ryoo and Jun, 1999) is highly encouraging for the exploration of carbon particles because of their immense variety of applications like adsorbents, electrode materials, energy storage material, stationary phase in liquid chromatographyand catalyst supports etc., The utilization of bio-waste materials based carbon modified solid catalysts is the one of the attractive tool in the field of catalysis due to inexpensive, eco-friendlier, high selectivity, easy separation and reusability compared to non-biomass based catalysts. Herein, we wish to deliver the synthesis of novel azo fused dipyrazolopyridine derivatives via one pot pseudo six component reaction using waste orange peel derived carbon modified sulfonic acid (C-SO_3H) catalyst.

2. RESULTS & DISCUSSION

2.1 Characterization of prepared C-SO_3H catalyst:

FT-IR analysis:

The broad vibration band at 3415 cm^{-1} is indicating the –OH stretching vibrations of sulfonic acid moieties, the bands at 1636 cm^{-1} and 1029 cm^{-1} representing the presence of asymmetric and symmetrical stretching modes of SO_2 which shows the presence of sulfonic acid groups in OPC-SO_3H material. The **powder X-ray diffractogram:** A broad peak at the diffraction mode of $2\theta = 25°$, which is attributed to the amorphous nature of the prepared OPC-SO_3H material.

SEM

Images indicate the prepared catalyst was in agglomerated structure. **EDAX** spectrum shows the elemental composition of the C-SO_3H (Carbon= 54.39%, Oxygen= 38.36% and Sulfur= 7.25%).**XPS** spectrum shows the binding energy of elements presented in the surface of C-SO_3H (Carbon=283.6 eV, Sulfur= 168.35 eV, and Oxygen= 531.15 eV).

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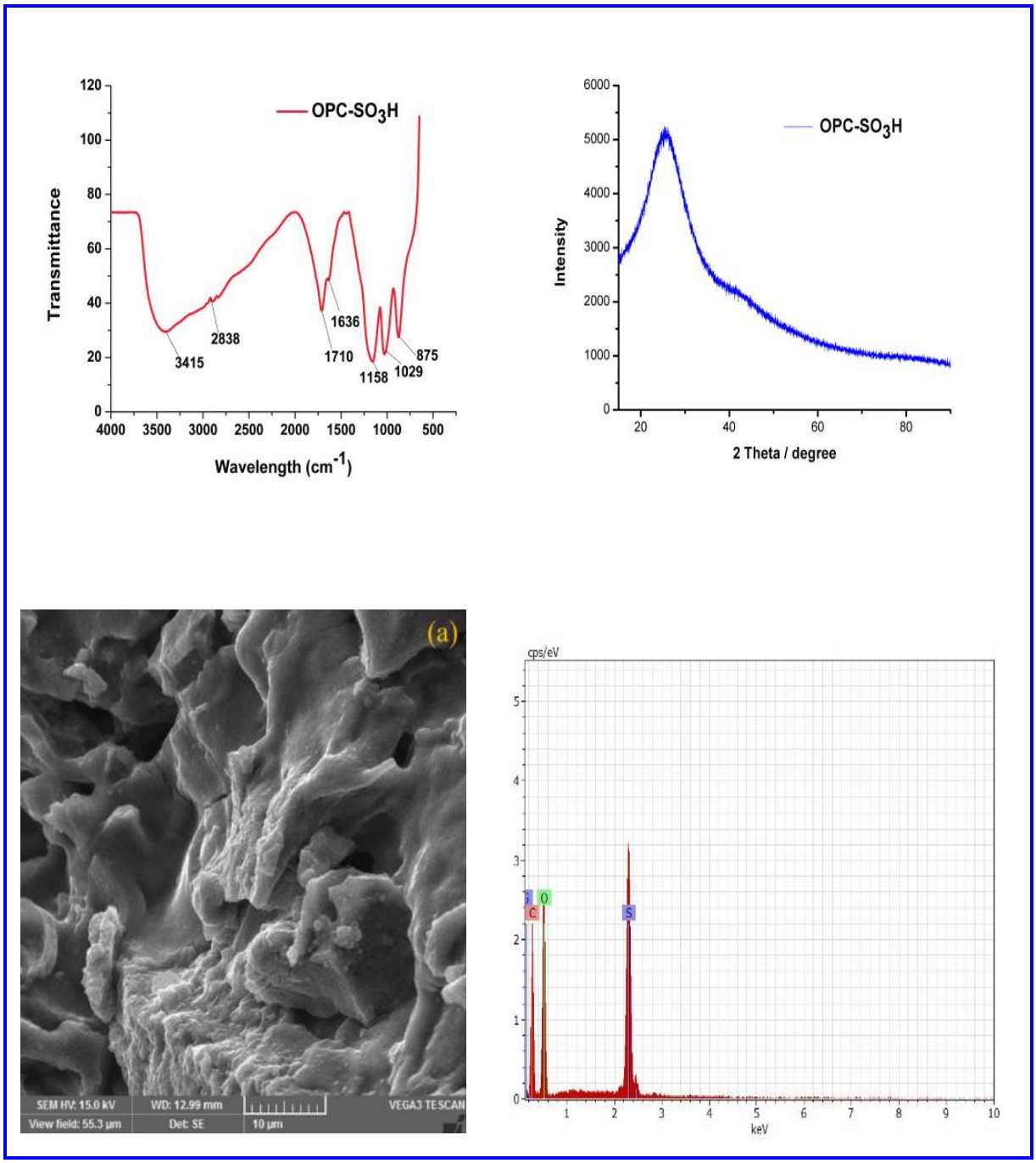
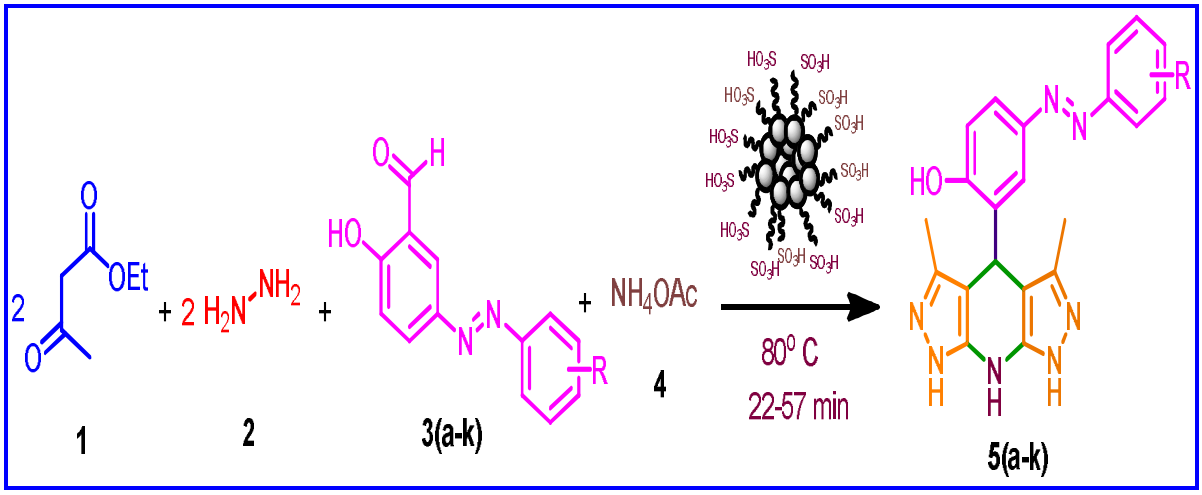


Fig. 1: Characterization of C-SO_3H material (a) FT-IR (b) XRD (c) SEM (d) EDAX (f) XPS.

2.2 Catalytic activity

We have attempted to explore the catalyst efficacy of OPC-SO_3H nano-powder by the experimentation with pseudo six-component reaction of ethyl acetoacetate **1** (2.0 mmol), hydrazine hydrate **2** (2.0 mmol), various substitute aryl azosalicyclaldehydes**3a-k** (2.0 mmol) and ammonium acetate **4** (2.0 mmol) using 20mg of C-SO_3H catalyst in ethanol solvent at refluxing temperature leading to the formation of novel tetrahydrodipyrazolopyridin-4-yl)-4-(phenyldiazenyl)phenol **(5a-k).** In addition, we have optimized the reaction conditions using various solvents and temperatures for obtaining better reaction time and targeted yields.



Scheme 1. Synthesis of novel azo fused tetrahydrodipyrazolo-4yl)-4-(aryldiazenyl)phenol derivatives using C-SO_3H catalyst[a].

Entry	Aldehyde	Product	Time (min)	Yield (%)[b]	Melting point (°C)
1	H	5a	24	90	Above 300
2	4-Cl	5b	22	92	218-220
3	3-Cl	5c	27	87	Above 300
4	2-Cl	5d	22	90	294-296
5	4-F	5e	25	85	Above 300
6	4-Br	5f	29	92	220-222
7	4-NO2	5g	37	86	Above 300
8	3-NO2	5h	26	90	254-256
9	4-OCH3	5i	27	89	Above 300
10	4-CH3	5j	39	92	Above 300

[a]Reaction conditions: ethyl acetoacetate (4.0 mmol), hydrazine hydrate (4.0 mmol), ammonium acetate (4.0 mmol) and differentsubsituted 5-arylazo salicylaldehyde (2.0 mmol) with C-SO_3H (20 mg) at 80 °C. [b]Isolated yields

3. CONCLUSION

In summary, C-SO_3H powder catalyst was designed and developed via simple pyrolysis followed by sulfonation process and it was utilized as a greener inexpensive heterogeneous catalyst for the synthesis of novel azo fused dipyrazolopyridine derivatives via a one pot pseudo six component reaction. The prepared catalyst was reused upto 7 cycles without loss of its activity.

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